

Tethered Indenyl–Phosphine Complexes of Ruthenium(II) via Reductive Elimination of a Ruthenium(IV) Complex

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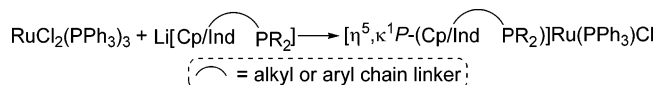
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The Ru(IV) phosphine complex $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})\text{RuCl}_2(\kappa^1\text{P-LH})]$ (**2**) was synthesized from the reaction of $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})\text{RuCl}_2]_2$ with $[(\text{C}_9\text{H}_7)(\text{CH}_2)_2\text{PPh}_2]$ (**LH**). Treatment of **2** with acid led to halide labilization to give $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})\text{RuCl}(\text{CH}_3\text{CN})(\kappa^1\text{P-LH})]^+$ [**2a**]⁺. Reductive elimination of the bis(allyl) ligand in **2** was effected in the reaction of **2**, a two- or four-electron ligand (DD), Na₂CO₃, and KPF₆ in EtOH, resulting in the isolation of PF₆ salts of monocationic tethered indenyl Ru species, $[(\eta^5, \kappa^1\text{P-L})\text{Ru}(\text{DD})]$ (**3**, DD = 1,5-cyclooctadiene (COD); **6**, DD = 2,2'-bipyridyl (bpy)), and neutral tethered indenyl Ru complexes (**4**, DD = (PPh₃)Cl; **5**, DD = (PPh₃)H). In addition to $[\text{6}]\text{PF}_6$, $[(\kappa^1\text{P-LH})\text{Ru}(\text{bpy})_2\text{Cl}]\text{PF}_6$, $[\text{7}]\text{PF}_6$, was an additional product in the bpy reaction, as was $\{[(\kappa^1\text{P-LH})\text{Ru}(\text{bpy})\text{Cl}]_2(\mu\text{-Cl})_3\}\text{PF}_6$, $[\text{8}]\text{PF}_6$, when Na₂CO₃ was replaced by Li₂CO₃. In the presence of HCl, $[\text{6}]^+$ was found to convert to $[\text{8}]^+$, while $[\text{8}]^+$ was converted to $[\text{7}]^+$ with bpy and KPF₆. The reaction of **2** with acetylacetone (acacH) gave a high yield of an unusual complex, $[(\eta^2, \kappa^1\text{P-LH})\text{Ru}(\text{acac})_2]$ (**9**), in which **LH** adopts a rare $\eta^2, \kappa^1\text{P}$ -coordination mode. The new compounds were all spectroscopically characterized, with **2**, **2a**, **3**, **4**, and **9** also determined by single-crystal X-ray diffraction analyses.

Introduction

Compared to their parent Cp/Ind systems, organometallic complexes containing tethered cyclopentadienyl ($\eta^5\text{-C}_5\text{H}_5$, Cp) or indenyl ($\eta^5\text{-C}_9\text{H}_7$, Ind) ligands can exhibit quite different stability and reactivity characteristics,¹ including catalytic activity.² This has stimulated much work directed at the synthesis of ligands with variations on the Cp ring, the spacer, the heteroatom donor, and its substituent.^{1e,3–6} Of keen interest is the combined effect of both metal-centered chirality and planar-chirality of Cp/Ind ligands on diastereoselectivity in reactions.^{5,7,8} Planar-chirality can be induced by nonsymmetrical ring

Scheme 1



substitution, advantageously with a tethered ligand for asymmetric syntheses, or by an optically active substituent (e.g., neomenthyl or neoisomenthyl) in the Cp ring or the tether.^{5b,c}

Since half-sandwich ruthenium complexes containing phosphine ligands are known to possess high catalytic activity for many reactions,⁹ tethered Cp analogues have been of special interest. Indeed, the literature to date contains many examples of such phosphine-containing ruthenium(II) species, originating from the ruthenium precursor $\text{RuCl}_2(\text{PR}_3)_3$ (Scheme 1).^{1b,3,5a,6} Recently, Takahashi reported the synthesis of tethered Cp–pyridine and –phosphine Ru(II) complexes containing acetonitrile co-ligands via displacement of a labile benzene ligand (Scheme 2a,c).⁷ These are useful precursors to desired derivatives, wherein the labile acetonitrile ligands are substituted by bidentate ligands such as 2,2'-bipyridine and dithiocarbamate (Scheme 2b,d). Shortly after, Salzer and co-workers prepared analogous acetonitrile complexes from the reactions of the dimeric ruthenium(IV) complex $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})\text{RuCl}_2]_2$ (**1**) in EtOH in the presence of CH₃CN and Li₂CO₃; the reaction occurred either via direct displacement of the 2,7-dimethylcyclooctadienediyl ligand with a Cp-linked phosphine ligand (Scheme

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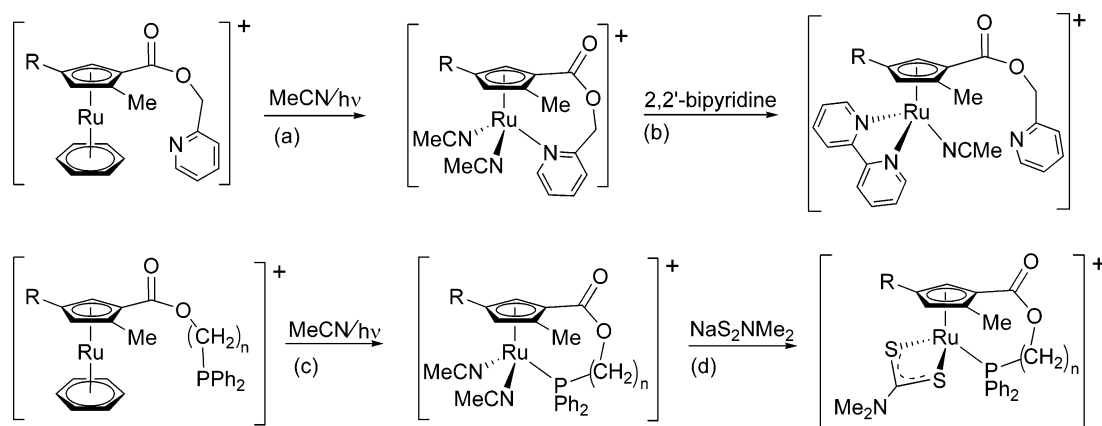
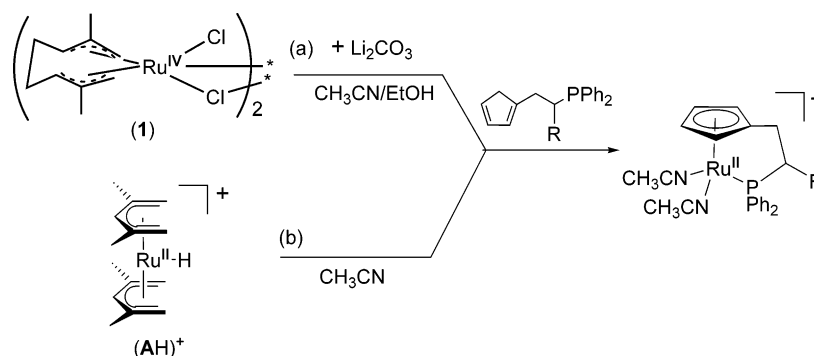
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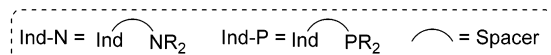
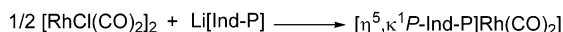
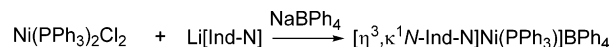
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Scheme 2

Scheme 3¹⁰

Scheme 4



3a)^{10a} or the reaction of the $[(\eta^5\text{-C}_7\text{H}_{11})_2\text{HRu}]^+(\text{AH})^+$ salt (obtained by protonation of **A**)¹¹ with the Cp-linked phosphine ligand in refluxing CH_3CN (Scheme 3(b)).^{10b}

In comparison to Cp-tethered transition metal complexes, their indenyl analogues are scarce, with those of Ni ,² Rh ,^{1e,5,8,12} and Ir ^{12c} being representative (Scheme 4). Enders had reported a stable complex of $\text{Cr}(\text{III})$ containing the Cp/Ind-N tether ($\text{N} = 8\text{-quinoline}$).^{12d}

A recently reported Ru complex bears a tethered indenyl ligand containing an amino group through constrained coordination.⁶ The relative scarcity of such tethered compounds is undoubtedly related to the lack of viable synthetic strategies. This study attempts to address the problem, and the results are described herein.

Results and Discussion

Synthesis. We tried route (b) in Scheme 3 using the Ind–phosphine ligand $\text{IndHCH}_2\text{CH}_2\text{PPh}_2$ (**LH**).^{5b} The reaction

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proved unsuccessful, giving an inseparable complex mixture of products. We next reacted **1** with **LH** at ambient temperature for 4 h. However, unlike Salzer's reaction with $\text{CpHCH}_2\text{CH}(\text{R})\text{PPh}_2$ or $\text{CpHCH}(\text{R}')\text{CH}_2\text{PPh}_2$,^{10a} an Ind–P tethered complex was not formed, but instead only a phosphine derivative of **1**, viz., complex **2**, in high yield (Scheme 5). It appears probable that the presence of bulky substituents (R or R') on the spacer carbons of the difunctional ligand predisposes the ligand toward tethering.

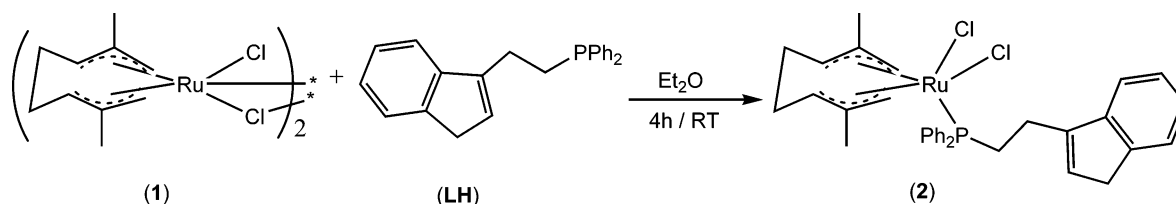
We therefore attempted to labilize the bis(allyl) ligand in **2** with an acid, the noncoordinating triflic acid, borrowing on the methodology of Werner and Stone in the use of carboxylic acids to labilize ruthenium–allyl bonds.¹³ However, this reaction led only to the precipitation of the triflic salt of $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})\text{RuCl}(\text{CH}_3\text{CN})(\kappa^1\text{-P-LH})]^+$, **[2a]**⁺, a solvento derivative of **2** (Scheme 6). The intact bis(allyl) ligand indicates its inertness to protonation. It is likely that further chloride substitution in **[2a]** CF_3SO_3 had been prevented by its insolubility in the solvent medium. A double dehalogenation at Ru had been postulated to be essential for C_5H_6 (CpH) or C_9H_8 (IndH) to coordinate to the metal.¹¹

The ¹H NMR spectra of **2** and **[2a]**⁺ are consistent with the presence of **LH** and the $(\eta^3, \eta^3\text{-C}_{10}\text{H}_{16})$ ligand. The ³¹P NMR spectrum of **2** shows a signal at δ 18.9, a typical chemical shift for a coordinated phosphine ligand. The ³¹P signal of **[2a]**⁺ is found in a lower field at δ 22.2.

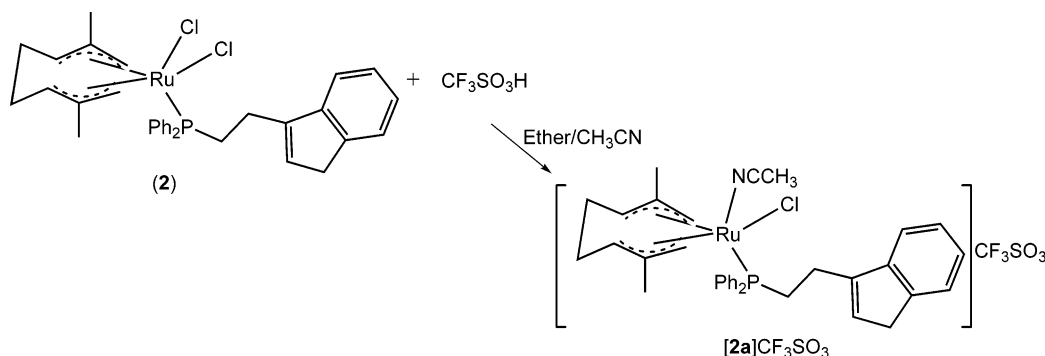
The ORTEP diagrams of **2** and **[2a]**⁺ are shown in Figure 1 and 2, respectively, and selected bond lengths and bond angles are given in Table 1. The X-ray structure of **2** shows that there are two independent molecules and one ether molecule in the

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Scheme 5



Scheme 6

Table 1. Selected Bond Lengths and Angles for 2 and [2a]⁺^a

bond length (Å)	2	[2a] ⁺	bond angles (deg)	2	[2a] ⁺
Ru(1)–P(1)	2.4144(11)	2.4050(16)	D(1)–Ru(1)–D(2)	130.51	130.87
Ru(1)–Cl(1)	2.4179(11)	2.4094(18)	D(1)–Ru(1)–Cl(1)	92.54	94.08
Ru(1)–X	X = Cl(2), 2.4331(11)	X = N(1), 2.031(6)	D(1)–Ru(1)–X	X = Cl(2), 88.23	X = N(1), 88.03
Ru(1)–C(12)	2.216(4)	2.274(6)	D(1)–Ru(1)–P(1)	114.63	115.08
Ru(1)–C(13)	2.295(4)	2.299(6)	D(2)–Ru(1)–Cl(1)	88.02	89.77
Ru(1)–C(14)	2.280(4)	2.252(6)	D(2)–Ru(1)–X	X = Cl(2), 92.01	X = N(1), 91.72
Ru(1)–C(17)	2.277(4)	2.201(6)	D(2)–Ru(1)–P(1)	114.85	114.04
Ru(1)–C(18)	2.275(4)	2.273(7)	Cl(1)–Ru(1)–X	X = Cl(2), 174.00(4)	X = N(1), 175.65(15)
Ru(1)–C(19)	2.231(4)	2.278(6)	Cl(1)–Ru(1)–P(1)	89.71(4)	84.42(6)
Ru(1)–D(1)	2.011	2.025	P(1)–Ru(1)–X	X = Cl(2), 84.56(4)	X = N(1), 91.24(15)
Ru(1)–D(2)	2.006	2.003	Ru(1)–P(1)–C(1)	115.82(15)	114.6(2)
C(3)–C(4)	1.326(7)	1.317(11)	C(2)–C(1)–P(1)	115.2(3)	115.3(4)
C(3)–C(11)	1.469(6)	1.501(12)			
C(4)–C(5)	1.490(7)	1.567(16)			
C(5)–C(6)	1.505(8)	1.473(18)			

^a D(1) and D(2) are the centroids of atoms C(12), C(13), C(14) and C(17), C(18), C(19), respectively.

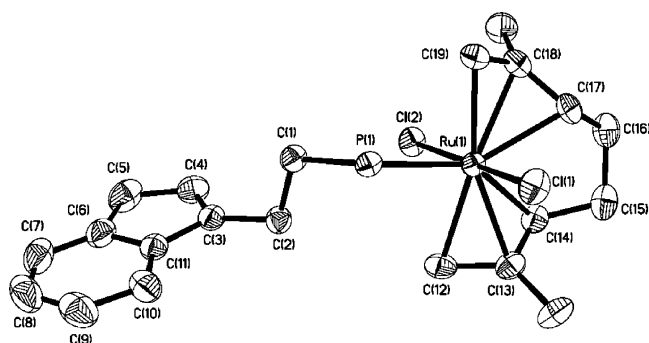


Figure 1. ORTEP diagram of 2 (50% probability thermal ellipsoids, hydrogen atoms and Ph rings have been omitted for clarity).

asymmetric unit, while the asymmetric unit of [2a]⁺CF₃SO₃⁻ contains one molecule of [2a]⁺ and a disordered CF₃SO₃⁻ anion. The molecular structures of 2 and [2a]⁺ are very similar to those of other reported bis(allyl) Ru(IV) complexes, e.g., RuCl₂(η³,η³-C₁₀H₁₆)P (P = Ph₂PNHC₆H₄PPh₂,¹⁴ Ph₂PNHNHpy¹⁵) and RuCl-

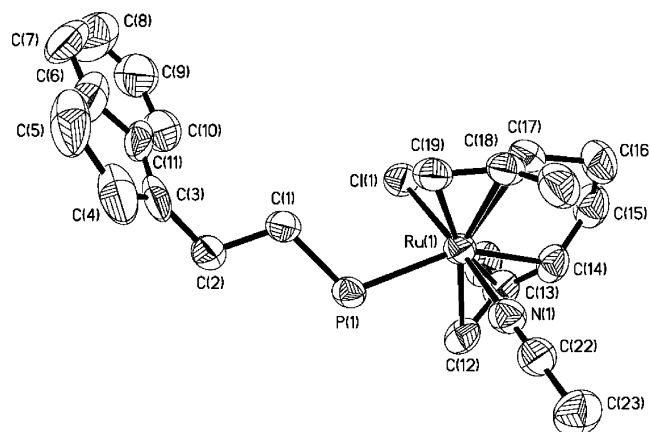


Figure 2. ORTEP diagram of 2a cation (50% probability thermal ellipsoids, hydrogen atoms and Ph rings have been omitted for clarity).

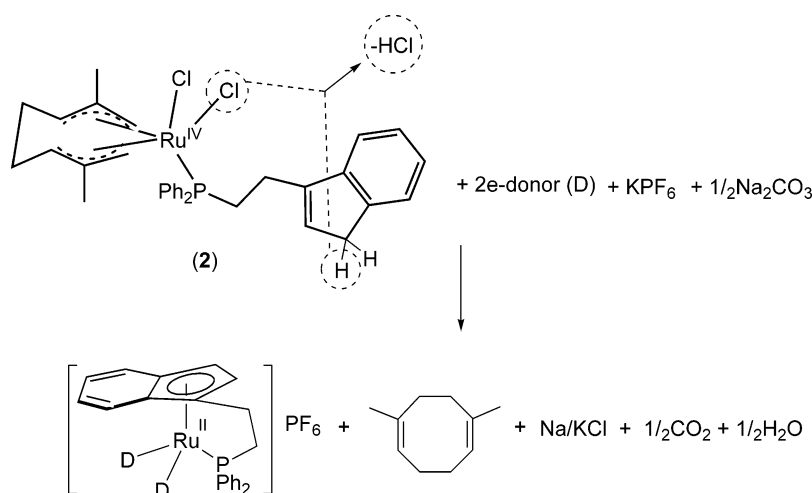
(η³,η³-C₁₀H₁₆)(CH₃CN)₂.¹⁶ The coordination geometries around the Ru center in both 2 and [2a]⁺ are distorted trigonal pyramidal, with bis(allyl) and the κ¹P-LH ligand occupying the equatorial positions. It was noticed that the phosphorus atom is

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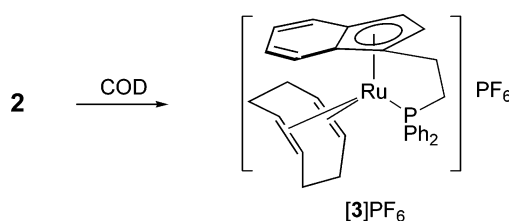
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Scheme 7



Scheme 8



almost equidistant from D1 and D2, the centroids of atoms C(12), C(13), C(14) and C(17), C(18), C(19), respectively, in **2**, while the phosphorus atom is closer to D2 than to D1 in [**2a**]⁺. The lack of symmetry in the bis(allyl) ligand in [**2a**]⁺ is reflected in the ¹H NMR spectroscopic data.

Subsequent to the above negative synthetic outcomes, we attempted reductive elimination of the bis(allyl) ligand in the presence of two- or four-electron donor ligands and a base or a halogen abstractor (Scheme 7). Indeed, we found that the reaction of **2** with 1,5-cyclooctadiene (COD) in the presence of AgPF₆ in EtOH solution proceeded at room temperature to give [(η⁵,κ¹P-L)Ru(COD)]PF₆, [**3**]PF₆, in high yield. The same result was obtained by refluxing **2** with COD in EtOH, in the presence of finely ground Na₂CO₃ and KPF₆ (Scheme 8). In fact this latter set of reagents has proven more useful, as it is compatible with different classes of incoming ligands, e.g., phosphine donors such as PPh₃, nitrogen donors such as 2,2'-bipyridyl, and oxygen donors such as acac, in which cases the Ag⁺ ion interferes. Additionally it was observed that the particle size of the base was a crucial factor on the yield, consistent with the heterogeneous nature of the reaction.¹⁷

The ¹H NMR signals for the COD ligand in [**3**]PF₆ appear in the range δ 0.66–2.20 for CH₂ and δ 3.52–4.04 for CH, while the protons of the ethylene side arm resonate as two multiplets in the range δ 2.32–2.89. The ³¹P signal appears at δ 67.7, which is within the low-field range [δ 52–88] reported for the tethered complex [(η⁵,κ¹P-Cp(CH₂)₂PPh₂)Ru(CH₃CN)₂]PF₆.^{10b}

The molecular structure of [**3**]⁺ showing the η⁵,κ¹P-coordination mode of **L** is illustrated in Figure 3. There is no significant difference between its bond parameters and those of its Ind analogue, [(η⁵-Ind)Ru(COD)(py)]BF₄.¹⁸ The slip-fold parameters for [**3**]PF₆ are (i) slip distortion (Δ) = 0.122 (7) Å, (ii) hinge

angle (HA) = 5.1°, and (iii) fold angle (FA) = 8.3°, indicating that the indenyl ligand is coordinated to the Ru center via a distorted η⁵-mode.¹⁹

The reactions of **2** with N-, P-, and O-donor ligands in the presence of 1 equiv of Na₂CO₃ in EtOH have been studied. The reaction with PPh₃ gave a mixture of [(η⁵,κ¹P-L)Ru(PPh₃-Cl)] (**4**) and [(η⁵,κ¹P-L)Ru(PPh₃)H] (**5**) (isolated in ca. 4:1 relative yield). Both **4** and **5** were obtained in only one diastereomeric form each. The formation of **5** was hindered by reducing the amount of Na₂CO₃; at zero or 0.5 mol equiv to **2**, none of **5** was formed, while the yield of **4** increased to 82%. A plausible formation pathway is proposed in Scheme 9, in which Na₂CO₃ is required for the functions of chloride and proton abstraction (routes (a) and (b), respectively). A separate reaction showed that complex **5** can be obtained in high yield

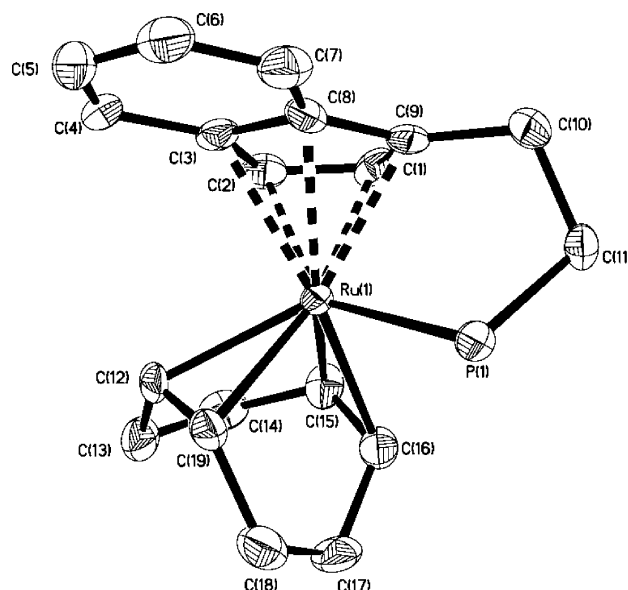
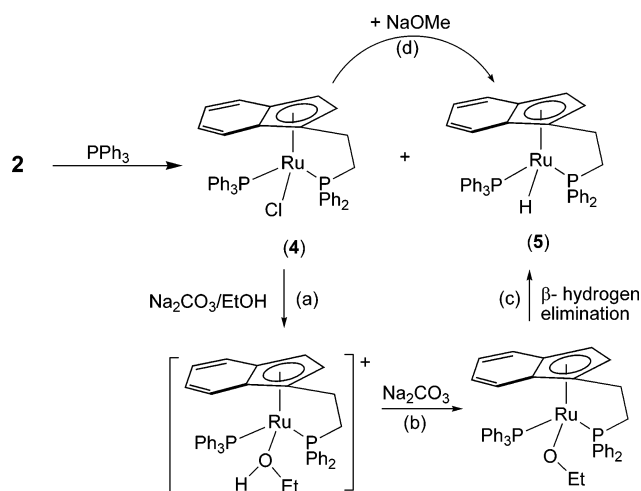


Figure 3. ORTEP diagram of [**3**]⁺ (50% probability thermal ellipsoids, hydrogen atoms and Ph rings have been omitted for clarity). Selected bond lengths (Å) and angles (deg). Ru(1)–P(1) = 2.3995(18); Ru(1)–C(12) = 2.223(6); Ru(1)–C(19) = 2.214(6); Ru(1)–C(15) = 2.212(7); Ru(1)–C(16) = 2.221(7); Ru(1)–C* = 1.911; C*–Ru(1)–C(12) = 115.62; C*–Ru(1)–C(15) = 112.24; C*–Ru(1)–C(16) = 141.12; C*–Ru(1)–C(19) = 137.55; C*–Ru(1)–P(1) = 107.88; C(15)–Ru(1)–C(16) = 37.2(2); C(12)–Ru(1)–C(19) = 36.4(3); Ru(1)–P(1)–C(11) = 100.0(2) (C* = centroid of the five-membered ring, comprising C(1), C(2), C(3), C(8), and C(9)).

(17) Salzer, A.; Bauer, A.; Geyser, S.; Podewils, F. *Inorg. Synth.* **2004**, 34, 59.

(18) Alvarez, P.; Gimeno, J.; Lastra, E.; García-Granda, S.; Van der Maelen, J. F.; Bassetti, M. *Organometallics* **2001**, 20, 3762.

Scheme 9

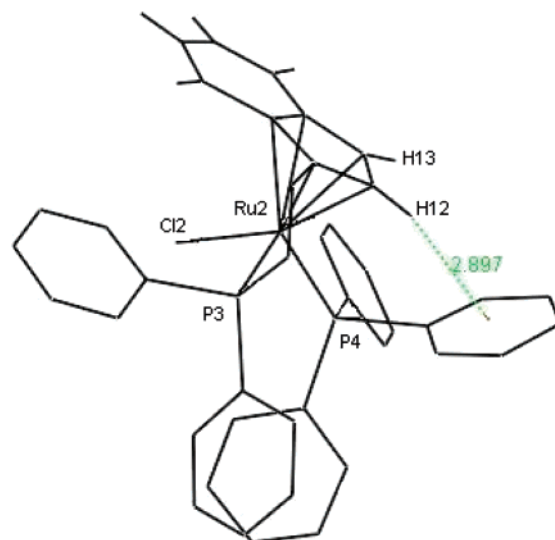


by refluxing **4** with NaOMe (pathway (d)). Hydride formation in thiolate substitution reactions of $(\text{Ind})\text{Ru}(\text{dppf})\text{Cl}$ had been shown to be effected by the generation of methoxide via an equilibrium between thiolate RS^- and MeOH ,^{20a} indeed, the synthesis of $(\text{Cp}/\text{Ind})\text{Ru}$ hydrides from halide precursors via methoxide intermediates is a standard methodology.^{20b–d}

The ^1H NMR spectrum of **4** shows five sets of multiplets in the range δ 1.42–3.22, assigned to the protons of the ethylene side arm of the **L** ligand. On the basis of a 2D-COSY NMR measurement, the two singlets at δ 2.26 and 4.87 are assigned to the protons on the five-membered ring of **L**. The upfield chemical shift (δ 2.26) of the protons on the Cp ring of the indenyl ligand had been observed at δ 3.56 in the tethered indenyl Ni complex, $[(\eta^5\text{-Ind}(\text{CH}_2)_2(\text{CH}=\text{CH}_2))\text{Ni}(\text{PPh}_3)\text{Cl}]$.^{2a,21} This is consistent with the X-ray structural analysis (see Figure 4), which shows the indenyl proton, H12, pointing directly toward the center of the phenyl ring and hence subjected to shielding by the ring current of the phenyl ring of PPh_3 .

The ^1H NMR spectrum of **5** shows a characteristic hydride signal at δ –13.9 as a doublet of a doublet, consistent with coupling to two P atoms of the phosphane ligands. The protons of the indenyl Cp ring resonate in the “normal” range at δ 4.78 and 5.48. This observation implies that the orientation of the Cp ring in **5** is different from that in **4**, but unfortunately X-ray crystal structural data could not be obtained.

The reaction of **2** with 1 molar equiv of 2,2'-bipyridyl (bpy) in the presence of Na_2CO_3 and KPF_6 led to the formation of $[(\eta^5, \kappa^1\text{-P-L})\text{Ru}(\text{bpy})]\text{PF}_6$ (**[6]PF₆**) and $[(\kappa^1\text{-P-LH})\text{Ru}(\text{bpy})_2\text{Cl}]\text{PF}_6$ (**[7]PF₆**) in ca. 2:1 molar ratio (Scheme 10(i)). An inverse relative yield (i.e., 1:2) of species **[6]PF₆** and **[7]PF₆**, was obtained when Na_2CO_3 was replaced by Li_2CO_3 ; in addition, a new product, $\{[(\kappa^1\text{-P-LH})\text{Ru}(\text{bpy})\text{Cl}]_2(\mu\text{-Cl})_3\}\text{PF}_6$, **[8]PF₆**, was formed (Scheme 10(ii)). The glaring difference in the composition of these complexes is the presence of chloride in **[7]PF₆**

Figure 4. Molecular structure of **4**.

and **[8]PF₆** and its absence in **[6]PF₆**. A very plausible rationale for the difference in the two situations therefore lies in the greater availability of chloride ions in the Li_2CO_3 case, arising from the higher solubility of LiCl versus NaCl in EtOH . This also explains the additional formation of species **[8]PF₆** with even higher Cl^- content. The supply of Cl^- from HCl was found to convert complex **[6]PF₆** completely to complex **[8]PF₆**, (Scheme 10(iii)), but this conversion could not be effected with NaCl . **[6]PF₆** with HCl converted to a mixture of complexes **[7]PF₆** and **[8]PF₆** in the added presence of 1.5 molar equiv of bpy (Scheme 10(iv)). In addition it was found that in the presence of 1 molar equiv of bpy and KPF_6 , **[8]PF₆** was transformed to **[7]PF₆** (Scheme 10(v)). It was also observed that the reaction of **2** with a 4-fold excess of bpy resulted in total displacement of all the ligands, giving $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ as the sole product. In context, we note that Salzer and co-workers had observed a marked effect of the carbonate bases of group 1 metals ($\text{Li} > \text{Na} > \text{K}$) on the yield of the sandwich bis(dienyl) complex $[(\eta^5\text{-C}_7\text{H}_{11})_2\text{Ru}]$ (**A**) from the reaction of **1** with dimethylpentadiene; this had been ascribed to solubility differences of the solid bases in the reaction medium.¹¹

The proposed formulations of species **[6]PF₆**, **[7]PF₆**, and **[8]PF₆** were based on microanalytical and spectroscopic evidence. The coordination mode of **L** and **LH** in the cationic complexes **[6]PF₆**, **[7]PF₆**, and **[8]PF₆** can be determined by their resonances in the ^1H NMR spectra. The protons of the Cp ring of $(\eta^5, \kappa^1\text{-P-L})$ in **[6]PF₆** appear at δ 5.21 and 5.53, indicating the aromaticity at the Cp ring, while the protons of the five-membered ring of $(\kappa^1\text{-P-LH})$ in species **[7]PF₆** and **[8]PF₆** are found at δ 6.10 (for the “-ene” proton) and δ 3.23 (for the sp^3 -protons). The ^{31}P NMR spectrum also gave significant insight into the coordination mode of the ligand as the ^{31}P signal of $(\eta^5, \kappa^1\text{-P-L})$ in **[6]PF₆** resonates at δ 61.7, which is at lower field than the ^{31}P signal of $(\kappa^1\text{-P-LH})$ in **[7]PF₆** (δ 39.5) and **[8]PF₆** (δ 54.5). Their mass spectra showed their mother ion peaks. While the isotopic distribution patterns of the signals showed that **[6]PF₆** and **[7]PF₆** are mononuclear species, that of **[8]PF₆** indicated a dinuclear species.

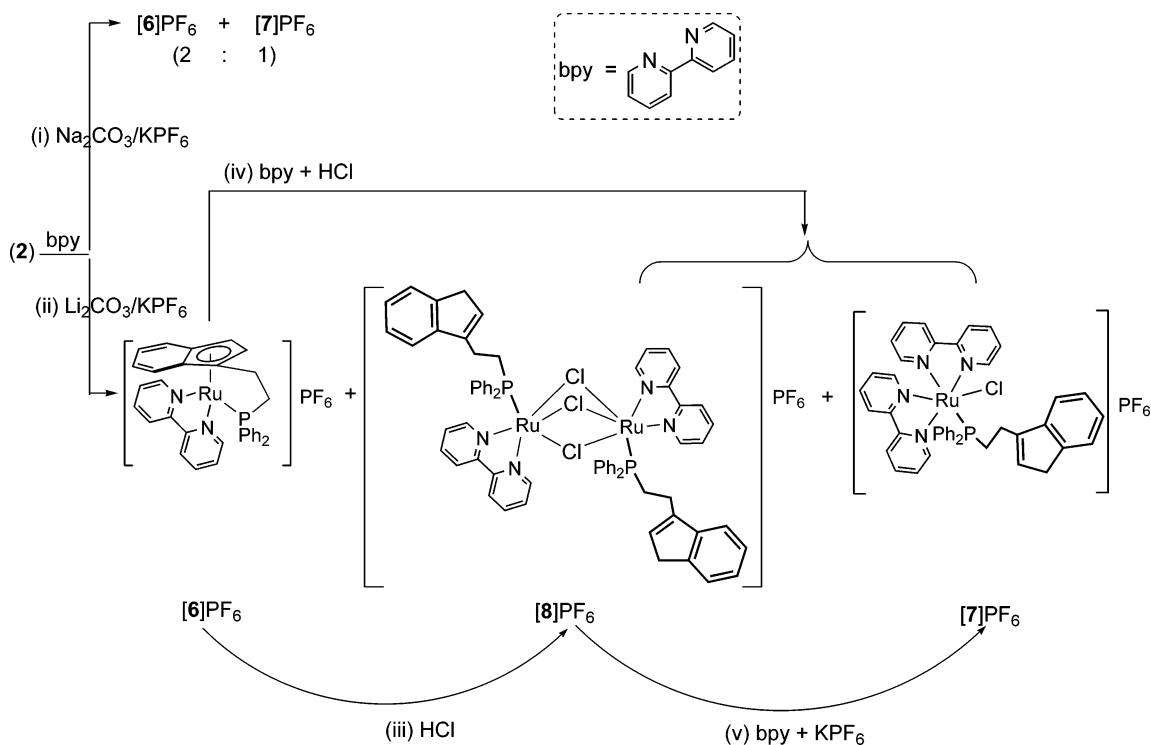
The reaction of **2** with 1 molar equiv of acetyl acetone in the presence of 2 molar equiv of Na_2CO_3 gave a multicomponent product mixture from which complex $[(\eta^2, \kappa^1\text{-P-LH})\text{Ru}(\text{acac})_2]$ (**9**) was isolated in 38% yield (Scheme 11). A repeat experiment

(19) For indenyl complexes containing undistorted η^5 rings: $\Delta = 0.03$ Å; $\text{HA} = 2.5^\circ$; $\text{FA} = 4.4^\circ$; for those containing distorted η^5 rings: $\Delta = 0.11\text{--}0.42$ Å; $\text{HA} = 7\text{--}14^\circ$; $\text{FA} = 6\text{--}13^\circ$; and for those wherein the five-membered ring is η^3 -coordinated: $\Delta = 0.8$ Å; $\text{FA} = 28^\circ$. See: Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, 198–200, 219.

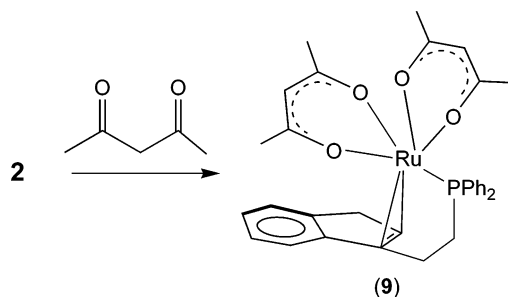
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Scheme 10



Scheme 11



using the correct stoichiometric amount of acetyl acetone to **2** in the presence of an appropriate molar equivalent of Na_2CO_3 gave an increased yield of **9** (78%) from a cleaner product mixture. In complex **9**, the Ru(II) center is coordinated to two chelating acac ligands and an **LH** ligand in an uncommon $\eta^2, \kappa^1 P$ -coordination mode.

Complex **9** was characterized by single-crystal X-ray diffraction analysis. The asymmetric unit contains two independent tilted molecules, the structures of which are very similar. This is shown in Figure 5, with selected bond parameters for one of the molecules. The Ru(II) center adopts a pseudo-octahedral geometry, with coordination to the four O atoms of two acac ligands, a P donor atom, which with O(4) occupies equatorial positions, and an “ene” C(1)–C(9) moiety taking up the sixth position, which is axial and trans to O(3). The $(\eta^2, \kappa^1 P\text{-LH})$ coordination mode to Ru is rare and had been observed before only in the $(\eta^2, \kappa^1 N\text{-Ind-quinolyl})$ tethered complexes of Rh(I) and Mo(0).²² Ethene complexes of acac-containing Ru(II) are known, e.g., *cis*-Ru(acac)₂($\eta^2\text{-C}_2\text{H}_4$)₂ (**B**) and derivatives thereof.²³ The bonding mode in **9** bears a slight resemblance to that found in $[(\eta^5\text{-Ind})\text{Ru}(\kappa^3(P, C, C)\text{-Ph}_2\text{P}(\text{CH}_2\text{CH}=\text{CH}_2))(\text{PPh}_3)]^+$ (**C**), in

which Ru is coordinated to P and the terminal alkene of a phosphino ligand;²⁴ the phosphine is homoallylic in **9** but allylic in the latter. The C(1)–C(9) bond length (1.392(4) Å, clearly of double-bond character, is close to that in **C** (1.391(8) Å)²⁴ but longer than those in coordinated unsubstituted ethenes in **B** and its monoethene derivatives (range 1.35(1)–1.37(3) Å).²³ The Ru(1)–P(1) distance is substantially shorter ($\Delta \approx 0.06\text{--}0.09$ Å) than the analogous distance in **C**.²⁴ The Ru(1)–C(1) distance is comparable to the equivalent distances in **B**;²³ however the Ru(1)–C(9) bond is significantly longer ($\Delta =$

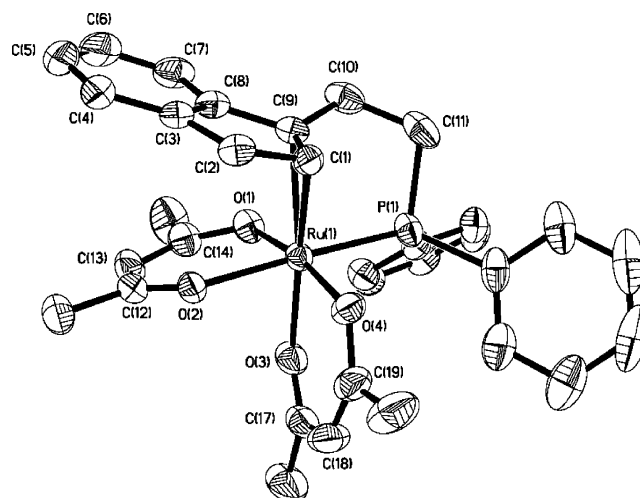


Figure 5. ORTEP diagram of **9** (50% probability thermal ellipsoids, hydrogen atoms omitted) and selected bond lengths (Å) and angles (deg): Ru(1)–O(1) = 2.0563(19); Ru(1)–O(2) = 2.1067(18); Ru(1)–O(3) = 2.069(2); Ru(1)–O(4) = 2.0670(19); Ru(1)–P(1) = 2.2495(8); Ru(1)–C(1) = 2.186(3); Ru(1)–C(9) = 2.252(3); C(1)–C(9) = 1.392(4); C(1)–C(2) = 1.513(4); O(1)–Ru(1)–O(2) = 90.23(8); O(3)–Ru(1)–O(4) = 89.53(9); C(1)–Ru(1)–C(9) = 36.53(10); C(1)–C(9)–C(8) = 107.3(2); C(1)–C(9)–C(10) = 128.2(3); C(8)–C(9)–C(10) = 119.4(2); C(9)–C(1)–C(2) = 110.7(2); C(9)–C(1)–Ru(1) = 74.32(16); C(2)–C(1)–Ru(1) = 113.82(19).

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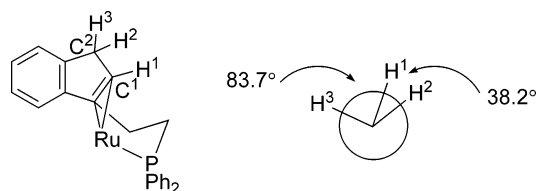


Figure 6. Hydrogen atoms-labelling of the indenyl 5-membered ring of **9**.

0.066 Å), understandably an effect of the asymmetry of the ethene moiety with higher steric constraint at bridgehead-like C(9). In contrast, complex **C** shows only a small difference in the Ru–C bonds of the metal center to the ethene moiety. While the Ru(1)–O distances in **9** (range 2.0563(19)–2.1067(18) Å) are similar to those in Bennett's Ru(acac) complexes, the Ru(1)–O(2) bond is substantially longer ($\Delta \approx 0.04$ –0.05 Å), rationalized as a consequence of the trans effect of the P donor atom.

The spectroscopic data of **9**, obtained from a proton NMR scan and a 2D-COSY experiment, are consistent with the structure. Thus, the proton spectrum shows the four chemically inequivalent Me groups of the two acac ligands at δ 1.34–1.80 and the allylic protons at δ 4.29 and 4.96. The protons on C10 and C11, the ethylene side arm, appear as four sets of multiplets in the range δ 2.32–2.89. Referring to the atom-labeling code shown in Figure 6, the “ene” proton (H¹ on C1) of the five-membered ring of Ind appears as a doublet at δ 5.15 with $^3J_{\text{HH}} = 3.7$ Hz (coupling with H²), while the sp³-protons H² on C2 appears as a doublet of a doublet at δ 3.39 ($^3J_{\text{HH}} = 3.7$ Hz and $^2J_{\text{HH}} = 20$ Hz) and H³ appears as a doublet at δ 3.61 ($^2J_{\text{HH}} = 20$ Hz; coupling with H²). The correlation of each signal was established using 2D-COSY NMR spectroscopy. There was no coupling observed between H³ and H¹. This observation was further supported by the X-ray structure, which shows that H¹ and H³ are almost orthogonal (83.7°) and therefore will have minimal transmission of nuclear spin information, resulting in no coupling, according to Karplus rule.²⁵ The angle between H² and H³ is 109.2°, with a geminal coupling constant of 20 Hz, which is slightly larger than the $^2J_{\text{HH}}$ of a typical sp³ protons on a C₆ ring with angle between the protons of $\sim 109^\circ$.²⁵

The formation of the Ru(II) complex **9** had involved multiple processes, viz., chloride abstraction from **2** by Na⁺ ions, followed by coordination of two acac[−] ligands with displacement of the bis(allyl) ligand. This so-formed 16-electron “intermediate” would not be able to accept a η^5 -indenyl ligand, unless one of the acac ligands can be displaced. That this had not occurred is consistent with the relative bond strength of the acac[−] versus η^5 -ind ligands. The metal center of the “intermediate” therefore achieves its 18-electron configuration by coordinating to the “ene” moiety of the LH ligand, giving rise to a ($\eta^2, \kappa^1 P$ -) bonding mode at Ru(II).

Attempts to synthesize the ($\eta^5, \kappa^1 P$ -L)Ru(II) complex with labile CH₃CN ligands were in vain, as refluxing **2** in a solvent mixture of EtOH/CH₃CN (1:1), Na₂CO₃, and KPF₆ led only to an inseparable complex mixture, indicating the need of strong donor ligands to stabilize ($\eta^5, \kappa^1 P$ -L)Ru(II) complexes.

Conclusion

A synthetic route has been developed for the transformation of bis(allyl)Ru(IV) precursor **2** to tethered [($\eta^5, \kappa^1 P$ -L)Ru(II)]

complexes containing COD, PPh₃, and 2,2'-bipyridyl ligands. While **L** adopts the expected $\eta^5, \kappa^1 P$ -coordination mode in complexes [**3**]⁺, **4**, **5**, and [**6**]⁺, it was also found to coordinate either via a $\kappa^1 P$ -LH, as in [**7**]⁺ and [**8**]⁺, or via a rare $\eta^2, \kappa^1 P$ -LH coordination mode, as found in **9**. The reaction methodology used here could be a potentially convenient route to more examples of tethered indenyl Ru derivatives.

Experimental Section

General Procedures. All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or under argon in an M. Braun Labmaster 130 inert gas system.

NMR spectra were measured on a Bruker 300 FT NMR spectrometer, while that of **9** and the 2D-COSY spectra of **4** and **9** were recorded on a Bruker 500 FT NMR spectrometer; for ¹H and ³¹P spectra, chemical shifts were referenced to residual solvent in the deuteriosolvents C₆D₆ and (CD₃)₂CO. IR spectra in KBr pellets were measured in the range 4000–400 cm^{−1}, using a BioRad FTS-165 FTIR instrument. Mass spectra were run on a Finnigan Mat 95XL-T (FAB) or a Finnigan-MAT LCQ (ESI) spectrometer. Elemental analyses were performed by the microanalytical laboratory in-house.

[(C₁₀H₁₆)RuCl₂]₂ (**1**)¹⁷ and IndH(CH₂)₂PPh₂ (LH)^{5b} were prepared by published methods. All other chemicals were obtained commercially and used as supplied. All solvents were dried over sodium/benzophenone and distilled before use. Celite (Fluka AG), silica gel (Merck Kieselgel 60, 230–400 Mesh), and neutral alumina (activity III) were dried at 140 °C overnight before chromatographic use. **Synthesis of [(η^3, η^3 -C₁₀H₁₆)RuCl₂($\kappa^1 P$ -LH)] (**2**).** **1** (100 mg, 0.16 mmol) was added into an ether solution of LH (106 mg, 0.32 mmol, 10 mL), and the suspension was stirred for 4 h, whereupon the color of the suspension changed slowly from purplish red to yellow. Yellow solids of **2** were filtered (93 mg, 45% yield). The filtrate was concentrated to ca. 1 mL, and hexane (ca. 5 mL) was added. A second crop of yellow microcrystals of **2** were obtained after 1 day at −30 °C (73 mg, 35% yield). Single crystals of X-ray diffraction quality were obtained from a solution of **2** in CH₂Cl₂ lacyerated with hexane after 2 days at −30 °C.

Data for **2.** ¹H NMR (CD₃CN): δ 2.15 (s, 6 H, Me), 2.24–2.38 (m, 2 H, IndH(CH₂)₂PPh₂), 2.50–2.60 (m, 2 H, IndH(CH₂)₂-PPh₂), 2.63–2.68 (m, 2 H, H^d and H^f), 3.12–3.14 (d-like, 2 H, H^b and Hⁱ), 3.29 (s, 2 H, H²⁻³), 3.39–3.45 (m, 2 H, H^e and H^g), 4.24–4.28 (d-like, 2 H, H^a and H^j), 5.12 (br s, 2 H, H^c and H^h), 6.26 (s, 1 H, H¹), 7.10–7.21, 7.42–7.49, 7.72–7.78, and 7.86–7.92 (each m, total 14 H, Ph and H⁴⁻⁷). ³¹P{¹H} NMR (CD₃CN): δ 18.9 (s, IndH(CH₂)₂PPh₂). FAB⁺-MS: *m/z* 636 [M]⁺, 601 [M − Cl]⁺, 565 [M − 2Cl]⁺, 464 [M − C₁₀H₁₆ − Cl]⁺, 429 [M − C₁₀H₁₆ − 2Cl]⁺. Anal. Calc (Found) for C₃₃H₃₇Cl₂PRu: C, 62.3 (62.1); H, 5.9 (6.0).

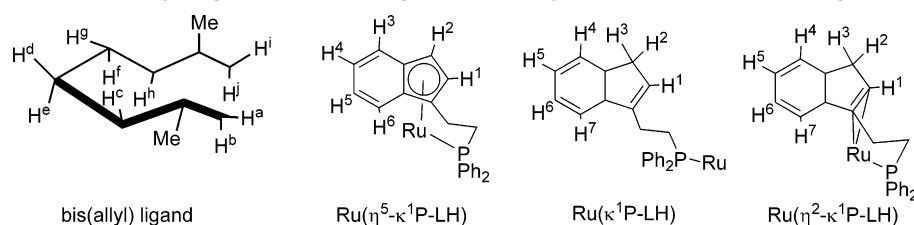
Synthesis of [(η^3, η^3 -C₁₀H₁₆)RuCl(CH₃CN)($\kappa^1 P$ -LH)](CF₃SO₃) (2a**·CF₃SO₃).** CF₃SO₃H (9 μ L, 0.10 mmol) was slowly injected into a stirred solution of **2** (30 mg, 0.047 mmol) in ether/CH₃CN (30:1, 10 mL), precooled to 0 °C. Yellow solids slowly precipitated out of the solution. The suspension was filtered after 1 h to give yellow solids of [**2a**]CF₃SO₃ (25 mg, 83% yield). Single crystals of X-ray diffraction quality were obtained from a THF solution with ether diffusion after 10 days at −30 °C.

Data for [2a**]CF₃SO₃.** ¹H NMR (CD₃CN): δ 1.67 and 2.27 (each s, 3 H, Me), 2.13–2.26 and 2.35–2.49 (each m, 1 H, IndH(CH₂)₂-PPh₂), 2.84 and 3.19 (each unresolved d, 1 H, IndH(CH₂)₂PPh₂), 2.74–2.80 (m, 2 H, H^d and H^f), 3.03–3.15 (m, 2 H, H^b and Hⁱ), 3.28 (s, 2 H, H²⁻³), 3.51–3.73 (m, 2 H, H^e and H^g), 4.28 and 4.40 (each d, *J* = 9.1 Hz, 1 H, H^a and H^j), 4.92–4.95 (d-like, 1 H, H^c or H^h), 5.32–5.36 (unresolved td, 1 H, H^c or H^h), 6.26 (s, 1 H, H¹), 6.89–6.92, 7.13–7.21, 7.42–7.44, 7.53–7.61, 7.75–7.81, and 7.98–8.04 (each m, total 14 H, Ph and H⁴⁻⁷). ³¹P{¹H} NMR (CD₃-

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Chart 1. Hydrogen Atom Labeling of the Bis(allyl) and Coordinated LH Ligands



CN): δ 22.2 (s, IndH(CH₂)₂PPh₂). IR (ν cm⁻¹, KBr): 3061 w, 2976 w, 2925 w, 2865 w, 2293 w (CN), 1437 m (CF₃SO₃), 1387 w (CF₃SO₃), 1265 vs (CF₃SO₃), 1223 m, 1151 s (CF₃SO₃), 1032 s (CF₃SO₃), 772 m, 753 m, 699 m, 638 s, 516 m. FAB⁺-MS: m/z 601 [M – CH₃CN]⁺, 565 [M – CH₃CN – Cl]⁺, 429 [M – CH₃CN – Cl – C₁₀H₁₆]⁺. Anal. Calc (Found) for C₃₆H₄₀ClF₃NO₃·PSRu: C, 54.6 (54.6); H, 5.1 (5.2); N, 1.8 (1.7).

Synthesis of [(η^5 , κ^1 P-L)Ru(COD)]PF₆, [3]PF₆, Method 1. COD (6 μ L, 0.063 mmol) was injected into a stirred suspension of **2** (30 mg, 0.047 mmol) and AgPF₆ (24 mg, 0.095 mmol) in EtOH (10 mL). After 2 h at RT, the suspension was filtered through Celite, giving a yellow filtrate. This was evaporated to dryness and the residue was crystallized from THF/hexane, giving orange-yellow microcrystals of [(η^5 , κ^1 P-L)Ru(COD)]PF₆, [3]PF₆ (27 mg, 84% yield).

Method 2. A yellow suspension of **2** (10 mg, 0.016 mmol), Na₂CO₃ (2 mg, 0.019 mmol), KPF₆ (3 mg, 0.016 mmol), and COD (2 μ L, 0.021 mmol) in EtOH (5 mL) was refluxed for 4 h. The yellow solids of **2** slowly dissolved upon heating. The solution was evacuated to dryness and extracted using THF. The extract was concentrated to ca. 1 mL, and hexane (ca. 3 mL) was added. Orange-yellow microcrystals of [3]PF₆ were obtained after 1 day at –30 °C (8 mg, 75% yield). Single crystals of X-ray diffraction quality were obtained from a CH₂Cl₂ solution layered with hexane after 3 days at –30 °C.

Data for [3]PF₆. ¹H NMR ((CD₃)₂CO): δ 0.66–0.77 (m, 1 H, COD), 1.28–1.45 (m, 2 H, COD), 1.83–1.98 (m, 2 H, COD), 2.13–2.20 (m, 2 H, COD), 2.32–2.54 (m, 2 H, Ind(CH₂)₂PPh₂), 2.60–2.89 (m, 2 H, Ind(CH₂)₂PPh₂), 3.52–3.62 (m, 1 H, COD), 3.74–4.04 (m, 4 H, COD), 5.01 (d, ³J_{HH} = 2.5 Hz, 1 H, H²), 5.12 (br m, 1 H, H¹), 6.70 (t, 1 H, H³⁻⁶), 7.00–7.03, 7.19–7.24, 7.42–7.48, 7.56–7.71, and 7.75–7.86 (each m, total 13 H, Ph and H³⁻⁶). ³¹P{¹H} NMR ((CD₃)₂CO): δ 67.7 (s, Ind(CH₂)₂PPh₂), –142.6 (septet, PF₆). IR (ν cm⁻¹, KBr): 2922 w, 2850 w, 1438 w, 1169 w, 1096 w, 836 vs (PF₆), 751 m, 704 m, 557 m (PF₆). FAB⁺-MS: m/z 537 [M]⁺, 429 [M – COD]⁺. Anal. Calc (Found) for C₃₁H₃₂F₆P₂Ru: C, 54.6 (54.7), H, 4.7 (4.8).

Synthesis of [(η^5 , κ^1 P-L)Ru(PPh₃)Cl] (4**). Method 1.** A yellow suspension of **2** (30 mg, 0.047 mmol), Na₂CO₃ (5 mg, 0.047 mmol), and PPh₃ (13 mg, 0.049 mmol) in EtOH (10 mL) was refluxed. The mixture changed to a dark brown homogeneous solution. After heating for 4 h, the solvent was removed under vacuum, and the residue was extracted with toluene (2 $\times$ 2 mL). The extract was concentrated to ca. 2 mL and then loaded onto a silica gel column (2 $\times$ 5 cm) prepared in *n*-hexane. Elution gave two fractions: (i) a yellow eluate in toluene (6–8 mL), which yielded [(η^5 , κ^1 P-L)Ru(PPh₃)H], **5** (5 mg, 15% yield; see synthesis below); (ii) a dark brown eluate in toluene/ether (1:1, 12–15 mL), which yielded dark brown crystals of **4** (20 mg, 58% yield) suitable for X-ray diffraction analysis, upon recrystallization from ether.

Method 2. A procedure similar to method 1 was adopted using 0.5 equiv of Na₂CO₃ (2.5 mg, 0.023 mmol). Dark brown crystals of **4** were obtained in 82% yield (28 mg), while **5** was not formed.

Data for **4.** ¹H NMR (C₆D₆): δ 1.42–1.52 and 1.52–1.64 (each m, 0.5 H, Ind(CH₂)₂PPh₂), 1.89–2.06 (m, 1 H, Ind(CH₂)₂PPh₂), 2.26 (s, 1 H, H¹), 2.78–2.91 and 3.10–3.22 (each m, 1 H, Ind(CH₂)₂PPh₂), 4.87 (s, 1 H, H²), 6.64–6.69, 6.79–6.83, 6.93–7.12,

7.25–7.28, 7.37–7.42, 7.68–7.72, and 8.02–8.07 (each m, total 29 H, Ph and H³⁻⁶). ³¹P{¹H} NMR (C₆D₆): δ 49.0 and 52.5 (each d, *J* = 26.7 Hz, PPh₃, Ind(CH₂)₂PPh₂). FAB⁺-MS: m/z 726 [M]⁺, 691 [M – Cl]⁺, 464 [M – PPh₃]⁺, 427 [M – Cl – PPh₃]⁺. Anal. Calc (Found) for C₄₁H₃₅ClP₂Ru: C, 67.8 (67.6); H, 4.9 (5.2).

Synthesis of [(η^5 , κ^1 P-L)Ru(PPh₃)H] (5**).** A brown mixture of **4** (10 mg, 13.8 mmol) and NaOMe (freshly generated from Na (2 mg, 87 mmol) in MeOH (5 mL)) in MeOH/THF (1:1, 10 mL) was refluxed for 2 h. The color of the mixture slowly changed from brownish-yellow to bright yellow. The solvent was evaporated to dryness and the residue extracted with hexane (2 $\times$ 4 mL). The hexane extract was concentrated to ca. 1 mL. Yellow solids of **5** (5 mg, 53% yield) were collected after 1 day at –30 °C.

Data for **5.** ¹H NMR (C₆D₆): δ –13.9 (dd, 1 H, *J* = 23.7, 40.3 Hz, Ru–H), 1.72–1.89 (m, 1 H, Ind(CH₂)₂PPh₂), 2.31–2.40 and 2.46–2.53 (each m, 0.5 H, Ind(CH₂)₂PPh₂), 3.07–3.18, 3.57–3.69 (each m, 1 H, Ind(CH₂)₂PPh₂), 4.78 and 5.48 (each s, 1 H, H¹ and H²), 6.40–6.43, 6.68–6.73, 6.76–6.84, 6.86–6.94, 7.01–7.08, 7.11–7.14, 7.51–7.54, and 7.91–7.97 (each m, total 29 H, Ph and H³⁻⁶), and δ 0.39 (s, H₂O). ³¹P{¹H} NMR (C₆D₆): δ 66.1 and 78.8 (each d, *J* = 23.7 Hz, PPh₃, Ind(CH₂)₂PPh₂). FAB⁺-MS: m/z 691 [M – H]⁺, 429 [M – PPh₃]⁺. Anal. Calc (Found) for C₄₁H₃₆P₂Ru·1.5H₂O: C, 68.5 (68.8), H, 5.5 (5.7).

Synthesis of [(η^5 , κ^1 P-L)Ru(2,2'-bipyridyl)]PF₆, [6]PF₆, and [(κ^1 P-LH)Ru(2,2'-bipyridyl)]ClPF₆, [7]PF₆. A yellow suspension of **2** (30 mg, 0.047 mmol), 2,2'-bipyridyl (8 mg, 0.051 mmol), Na₂CO₃ (5 mg, 0.047 mmol), and KPF₆ (9 mg, 0.049 mmol) in EtOH (10 mL) was refluxed. A red mixture resulted after 4 h. The solvent was removed under vacuum and the residue extracted using THF (2 $\times$ 5 mL). The extract was concentrated to ca. 2 mL and loaded onto a neutral alumina (activity III) column prepared in THF. Elution gave four fractions: (i) a yellow eluate in THF (2 mL); (ii) a red eluate in THF/acetone (4:1, ca. 25 mL), which gave [6]PF₆ as a red oil (20 mg, 58% yield); (iii) a red eluate in THF/acetone (1:1, ca. 8 mL), which gave [7]PF₆ (11 mg, 25% yield) as red solids upon recrystallization from CH₂Cl₂/ether (1:10); (iv) a red eluate in MeOH (ca. 1 mL), which gave a trace of an unknown species.

A similar reaction was repeated, using Li₂CO₃ (3.5 mg, 0.047 mmol) instead of Na₂CO₃. The ³¹P NMR spectrum of the reaction mixture showed the presence of the cationic species [6]PF₆, [7]PF₆, and [8]PF₆, in the ratio of 1:2:2. Separation of these complexes via silica gel chromatography was futile, as complexes [7]PF₆ and [8]PF₆ have similar polarity.

HCl (0.35 mL of 0.1 M) was added into a red solution of [6]PF₆ (5 mg, 0.007 mmol), and 2,2'-bipyridyl (1.6 mg, 0.01 mmol) in EtOH (0.5 mL) was refluxed for 2 h. The solvent was evaporated to dryness and the residue redissolved in *d*-acetone. ¹H and ³¹P NMR spectroscopy showed the total conversion to [7]PF₆ and [8]PF₆ in 2:1 ratio.

A red suspension of [8]PF₆ (4 mg, 0.003 mmol), 2,2'-bipyridyl (0.4 mg, 0.003 mmol), and KPF₆ (0.5 mg, 0.003 mmol) in EtOH (0.5 mL) was refluxed for 2 h. The resultant red solution was evaporated to dryness and redissolved in *d*-acetone. ¹H and ³¹P NMR spectroscopy showed the total conversion of species **8** to **7**.

Data for [6]PF₆. ¹H NMR ((CD₃)₂CO): δ 2.82–3.24 (m, 2 H, Ind(CH₂)₂PPh₂), 3.74–3.94 (m, 2 H, Ind(CH₂)₂PPh₂), 5.21 (d, ³J_{HH}

Table 2. Crystal and Structure Refinement Data

	2	[2a]CF ₃ SO ₃	3	4	9
formula	C _{33.50} H _{38.25} Cl ₂ O _{0.13} PRu	C ₃₆ H ₄₀ ClF ₃ NO ₃ PRuS	C ₃₂ H ₃₄ Cl ₂ F ₆ P ₂ Ru	C ₄₂ H _{37.50} ClO _{0.25} P ₂ Ru	C ₃₃ H ₃₅ O ₄ PRu
molecular weight	645.83	791.24	766.50	744.68	627.65
space group (cryst syst)	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
cryst syst	triclinic	monoclinic	triclinic	triclinic	monoclinic
unit cell dimens					
<i>a</i> (Å)	12.1186(4)	14.6702(8)	9.1518(5)	11.1768(12)	29.3586(12)
<i>b</i> (Å)	12.4772(5)	9.0353(5)	13.3458(8)	16.1725(17)	11.4964(4)
<i>c</i> (Å)	20.6703(8)	26.8742(15)	13.6837(8)	21.521(2)	17.9306(7)
α (deg)	90.5620(10)	90	69.821(2)	84.424(3)	90
β (deg)	101.7530(10)	99.9560(10)	75.8110(10)	81.268(3)	106.0200(10)
γ (deg)	96.6540(10)	90	81.523(2)	70.180(3)	90
cell volume (Å ³)	3037.5	3508.5(3)	1517.23(15)	3612.8(7)	5816.9(4)
<i>Z</i>	4	4	2	4	8
<i>D</i> _{calc} (g cm ⁻³)	1.412	1.498	1.678	1.369	1.433
absorp coeff (mm ⁻¹)	0.766	0.681	0.859	0.626	0.630
<i>F</i> (000) electrons	1333	1624	776	1530	2592
cryst size (mm ³)	0.28 × 0.16 × 0.14	0.60 × 0.20 × 0.14	0.14 × 0.10 × 0.04	0.10 × 0.06 × 0.02	0.30 × 0.20 × 0.16
θ range for data collection (deg)	2.01 to 29.09	1.48 to 25.00	1.62 to 25.00	0.96 to 25.00	0.72 to 27.50
index ranges	−16 ≤ <i>h</i> ≤ 15 −16 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 28	−17 ≤ <i>h</i> ≤ 16 −9 ≤ <i>k</i> ≤ 10 −31 ≤ <i>l</i> ≤ 31	−10 ≤ <i>h</i> ≤ 10 −15 ≤ <i>k</i> ≤ 10 −16 ≤ <i>l</i> ≤ 13	−13 ≤ <i>h</i> ≤ 13 −19 ≤ <i>k</i> ≤ 19 −25 ≤ <i>l</i> ≤ 25	−28 ≤ <i>h</i> ≤ 38 −14 ≤ <i>k</i> ≤ 14 −23 ≤ <i>l</i> ≤ 18
no. of reflns collected	40 877	19 971	9007	38 904	40 443
no. of indep reflns	14 685	6200	5337	12 708	13 340
max. and min. transmn	0.9003–0.8140	0.9107–0.6855	0.9665–0.8892	0.9876–0.9401	0.9059–0.8335
no. of data/restraints/ params	14 685/0/692	6200/42/420	5337/0/388	12 708/58/855	13 340/0/719
GoF	1.101	1.024	1.144	1.185	1.064
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0608	<i>R</i> 1 = 0.0672	<i>R</i> 1 = 0.0713	<i>R</i> 1 = 0.1359	<i>R</i> 1 = 0.0425
<i>R</i> indices (all data)	w <i>R</i> 2 = 0.1346 <i>R</i> 1 = 0.0834 w <i>R</i> 2 = 0.1447	w <i>R</i> 2 = 0.1708 <i>R</i> 1 = 0.1033 w <i>R</i> 2 = 0.1904	w <i>R</i> 2 = 0.1453 <i>R</i> 1 = 0.0898 w <i>R</i> 2 = 0.1537	w <i>R</i> 2 = 0.3149 <i>R</i> 1 = 0.1596 w <i>R</i> 2 = 0.3259	w <i>R</i> 2 = 0.0938 <i>R</i> 1 = 0.0547 w <i>R</i> 2 = 0.1021
largest diff peak and hole (e Å ⁻³)	1.122 and −0.801	1.071 and −0.524	1.174 and −0.963	2.991 and −1.541	0.919 and −0.356

= 2.5 Hz, 1 H, H²), 5.53 (m, 1 H, H¹), 6.82–6.94, 7.07–7.38, 7.44–7.49, 7.54–7.70, 7.80–7.91, 8.35–8.40, and 9.04–9.06 (each m, total 22 H, bipyridyl, Ph and H^{3–6}), and δ 1.80 and 3.62 (each m, THF). ³¹P{¹H} NMR ((CD₃)₂CO): δ 61.7 (s, Ind(CH₂)₂PPh₂), −142.6 (septet, PF₆). IR (ν cm⁻¹, KBr): 3054 w, 2923 w, 1436 w, 1265 w, 1161 w, 1096 w, 1029 w, 841 vs (PF₆), 745 w, 699 w, 558 w (PF₆), 518 w. FAB⁺-MS: *m/z* 585 [M]⁺, 429 [M − bipyridyl]⁺. Anal. Calc (Found) for C₃₃H₂₉F₆N₂P₂Ru·C₄H₈O: C, 55.3 (55.3); H, 4.6 (4.1); N, 3.5 (3.4).

Data for [7]PF₆. ¹H NMR ((CD₃)₂CO): δ 2.25–2.38 (m, 2 H, IndH(CH₂)₂PPh₂), 2.84–2.91 (m, 2 H, IndH(CH₂)₂PPh₂), 3.23–3.24 (m, 2 H, H^{2–3}), 6.10 (s, 1 H, H¹), 6.91–6.94, 6.96–7.01, 7.03–7.16, 7.24–7.28, 7.38–7.47, 7.52–7.57, 7.63–7.68, 7.78–7.83, 8.00–8.18, 8.23–8.29, 8.48–8.50, 8.64–8.70, 9.17–9.19, and 9.84–9.86 (each m, total 30 H, bipyridyl, Ph and H^{4–7}). ³¹P{¹H} NMR ((CD₃)₂CO): δ 39.5 (s, IndH(CH₂)₂PPh₂), −142.6 (septet, PF₆). IR (ν cm⁻¹, KBr): 3069 w, 2921 w, 1459 w, 1439 w, 1162 w, 1096 w, 1025 w, 842 vs (PF₆), 763 m, 558 w (PF₆), 521 w. FAB⁺-MS: *m/z* 777 [M]⁺, 449 [M − (LH)]⁺. Anal. Calc (Found) for C₄₃H₃₆ClF₆N₂P₂Ru·1/2CH₂Cl₂: C, 54.1 (54.2); H, 3.9 (4.2); N, 5.8 (6.2).

Synthesis of {[(κ^1 P-LH)Ru(2,2'-bipyridyl)]₂(μ -Cl)}PF₆ [8]-PF₆. HCl (0.7 mL of 0.1 M) was added into a red solution of [6]-PF₆ (10 mg, 0.014 mmol) in EtOH, and the solution was stirred at RT for 4 h. The resultant red solution was evacuated to dryness. The residue was dissolved in acetone and the solution passed through a short neutral alumina (activity III) column. Subsequent workup of the red eluate in acetone/ether (3:1) gave [8]PF₆ as crystalline red flakes (7 mg, 70% yield).

Data for [8]PF₆. ¹H NMR ((CD₃)₂CO): δ 2.48 (br s, 2 H, IndH(CH₂)₂PPh₂), 2.70–2.80 (m, 2 H, IndH(CH₂)₂PPh₂), 3.23 (s, 2 H, H^{2–3}), 6.10 (s, 1 H, H¹), 6.94–6.96, 6.99–7.04, and 7.76–7.81

(each td-like m, 1 H, bipyridyl), 7.13–7.35 and 7.38–7.44 (each m, total 14 H, Ph and H^{4–7}), 8.18–8.24 (t-like m, 2 H, bipyridyl), 9.08 and 9.18 (each d, ³J_{HH} = 4.9 Hz, 1 H, bipyridyl). ³¹P{¹H} NMR ((CD₃)₂CO): δ 54.5 (s, IndH(CH₂)₂PPh₂), −142.6 (septet, PF₆). FAB⁺-MS: *m/z* 1279 [M]⁺, 777 [M − Ru(LH)Cl₂]⁺, 585 [M − Ru(LH)(N₂C₁₀H₈)Cl₂]⁺, 465 [M − (LH)₂(N₂C₁₀H₈)]⁺, 429 [M − (LH)₂(N₂C₁₀H₈)Cl]⁺. HR-FAB⁺-MS for C₆₆H₅₆N₄Cl₃P₂Ru₂ [M]⁺: *m/z* 1278.1131 (found), 1278.1121 (calc). Anal. Calc (Found) for C₆₆H₅₆Cl₃F₆N₄P₃Ru₂: C, 55.8 (55.4); H, 4.0 (3.9); N, 3.9 (4.0).

Synthesis of [(η^2 , κ^1 P-L)Ru(acac)₂] (9). A yellow suspension of 2 (30 mg, 0.047 mmol), Na₂CO₃ (13 mg, 0.12 mmol), and acetyl acetone (12 μ L, 0.12 mmol) in EtOH (10 mL) was refluxed. As the reaction proceeded, a yellow mixture resulted. After refluxing for 4 h, the solvent was removed under vacuum and the residue extracted using hexane (2 × 5 mL). The extract was concentrated to ca. 2 mL and loaded onto a silica gel column (1 × 8 cm) prepared in *n*-hexane. Elution gave two fractions: (i) a yellow eluate in hexane/ether (6:1, 2 mL), which yielded <1 mg of a solid material, probably also of 9; (ii) a yellow eluate in hexane/ether (4:1, 8 mL), which upon recrystallization from hexane yielded yellow crystals of 9 (23 mg, 78% yield). X-ray diffraction-quality crystals were obtained from a concentrated hexane solution in an NMR tube after 1 h at room temperature.

Data for 9. ¹H NMR (CD₂Cl₂): δ 1.34 (s, 3 H, Me), 1.43 (s, 3 H, Me), 1.68 (s, 3 H, Me), 1.80 (s, 3 H, Me), 2.32–2.45 (m, 1 H, Ind(CH₂)₂PPh₂), 2.50–2.73 (m, 2 H, Ind(CH₂)₂PPh₂), 2.71–2.74 and 2.81–2.89 (each m, 0.5 H, Ind(CH₂)₂PPh₂), 3.39 (dd, *J* = 3.7, 20 Hz, 1 H, H²), 3.61 (d, *J* = 20 Hz, 1 H, H³), 4.29 and 4.96 (each s, 1 H, [(CH₃)C(O)]₂CH), 5.15 (d, *J* = 3.7 Hz, H¹), 6.91–6.97, 6.98–7.07, 7.09–7.22, 7.24–7.30, 7.34–7.45, and 7.96–8.03 (each m, total 14 H, H^{4–7}), and δ 0.89 and 1.23 (each m, hexane). ³¹P{¹H} NMR (CD₂Cl₂): δ 70.4 (s, Ind(CH₂)₂PPh₂). IR (ν cm⁻¹,

KBr): 3054 w, 2915 w, 2872 w, 2835 w, 1581 s (CO), 1513 vs (CO), 1435 m, 1395 s, 1261 w, 1196 w, 1097 w, 1019 w, 938 w, 855 w, 741 w, 698 m, 603 w, 528 m. FAB⁺-MS: *m/z* 628 [M]⁺, 528 [M – acac]⁺, 429 [M – 2 acac]⁺. Anal. Calc (Found) for C₃₃H₃₅O₄PRu•1/4C₆H₁₂: C, 63.8 (63.8); H, 5.9 (5.6).

Crystal Structure Determinations. Crystals were mounted on quartz fibers. X-ray data were collected on a Bruker AXS APEX system, using Mo K α radiation, with the SMART suite of programs.²⁶ Data were processed and corrected for Lorentz and polarization effects with SAINT²⁷ and for absorption effects with SADABS.²⁸ Structural solution and refinement were carried out with the SHELXTL suite of programs.²⁹ Crystal and structure refinement data are summarized in Table 2. The structures were solved by direct methods or Patterson maps to locate the heavy

atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model.

The crystal of **2** contained a diethyl ether solvent molecule with partial occupancy. This was modeled as disordered over an inversion center.

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Supporting Information Available: Complete crystallographic data in CIF format for **2**, **2a**, **3**, **4**, and **9** and ¹H NMR (500 MHz) spectrum of **9** showing signals of H^{1–3}. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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